

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 03 JUN 2005

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Applicant's or agent's file reference ACD 2995 WO		FOR FURTHER ACTION		See Form PCT/PEA/416
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International Patent Classification (IPC) or national classification and IPC C08F4/38, C08F14/06, C08F2/18, B01J19/00				
Applicant AKZO NOBEL N.V.				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 2 sheets, as follows:</p> <p><input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand 04.11.2004		Date of completion of this report 06.06.2005		
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer Kaumann, E Telephone No. +31 70 340-3640 		

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/004500

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-17 as originally filed

Claims, Numbers

1-9 received on 06.04.2005 with letter of 06.04.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/004500

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-9
	No: Claims	
Inventive step (IS)	Yes: Claims	1-9
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-9
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Subject-matter

Subject-matter of the present application is a process for the polymerisation of one or more monomers (preferably vinyl chloride) employing two polymerisation initiators of different reactivity, characterised by the amount and timing of the initiators' introduction being regulated such that the full cooling capacity of the polymerisation reactor is used. The second initiator has a half life time from 0,0001 to 1,0 hour at polymerization temperature. This second initiator is dosed at least partially after the start of the polymerization until 10 % of the monomer(s) has been polymerized in an amount that at least 92 % of the cooling capacity is used for at least a period of time wherein at least 10 wt-% of the monomer is polymerized.

The process supposedly improves the space-time yield of polymerisation, thus using the reactor under optimum conditions while, at the same time, avoiding the risk of run-away reactions (reactor overheating and auto-acceleration due to the released heat of reaction)

2. Problem and Solution

The problem to be solved was to provide a polymerization process showing improved the space-time-yield and avoids the risk of run-away reactions.

The claimed process appears to contribute a solution to this problem.

3. Prior Art

D1 = WO 00/17245 discloses a polymerization process of vinyl chloride monomers with peroxides. D1 relates to a suspension polymerization process using protective colloids. According to claim 1 of D1 one or more peroxides can be used. The only example where more than one peroxides are used is example F. In example F, Trigonox EHP and Triganox 187, which are also used in the examples of the present application, are used in an amount of 0,05 wt-% and 0,01 wt-%.

A distinguishing feature between example F of D1 and the subject-matter of the present claims is that, according to D1, the second initiator is dosed for one hour, starting 2,5 h after the start, while according to the claimed process the second initiator is dosed at least partly from the start until 10 % of the monomer(s) have been polymerized.

D2 = DE 30 29 211 discloses a vinyl chloride polymerisation using a catalyst mixture containing cumyl-permeodecanoate and a further peroxide group containing polymerisation initiator. The second initiator can be added batchwise or continuously.

Claim 7 of D2 discloses the use of a peroxide mixture which appears to fulfills the requirements of the present claims. On page 13, lines 6 to 9, D2 discloses that the described process is a contribution to the technical problem as described in the present application.

A distinguishing feature is that D2 does not disclose the details according to the claimed process. D2 does not disclose that at most 90 mole % of the safely usable amount of the first initiator should be used and that the second initiator is to be dosed at least partly after the start of the polymerization until 10 % of the monomer(s) has been polymerized, in an amount at preferably at a variable rate, such that at least 92% of the maximum cooling capacity is used during at least a period of time wherein at least 10% by weight of the monomer is polymerized.

Therefore, D2 is only considered a generic disclosure.

D3 = US 3,778,422 discloses the polymerisation of vinyl halide with a mixture of an organic peroxy dicarbonate and an alkyl hydroperoxide (see col 2, lines 67 - 71). The polymerization is carried out in suspension (see col. 3, lines 24 to 31 and examples).

A distinguishing feature is that the total amount of peroxide initiators is already incorporated in the initial reaction mixture. No polymerization is disclosed wherein a second initiator is dosed to the reaction mixture at least partially after the start of the polymerization.

D4 = EP 0 096 365 (cited in the application) discloses in examples 3 -7 a process for the polymerization of vinyl chloride using two different peroxy compounds. Claims 4 - 10 of D4 disclose the ratio between the two catalysts. A suspension polymerization using protective colloids is disclosed on page 9, line 30 to page 10, line 33.

A distinguishing feature is that D4 discloses a process where the entire initiator system is added to the polymerization system at the beginning and also a process where it is added in three parts. In this case it is reported that the system was overheated.

D4 does not disclose the details according to the claimed process. D4 does not disclose that at most 90 mole % of the safely usable amount of the first initiator should be used and

that the second initiator is to be dosed at least partly after the start of the polymerization, in an amount at preferably at a variable rate, such that at least 92% of the maximum cooling capacity is used during at least a period of time wherein at least 10% by weight of the monomer is polymerized.

Therefore, D4 is only considered a generic disclosure.

4. Article 33(2) PCT (Novelty)

In view of the distinguishing features, outlined above novelty can be acknowledged to the present claims.

5. Article 33(3) PCT (Inventive Step)

The present application does meet the criteria of Article 33(1) PCT, because the subject-matter of **claims 1 - 9** does involve an inventive step in the sense of Article 33(3) PCT. D1 is regarded as the closest prior art for the subject-matter of the present claims.

D1 disclose on page 2, lines 1 - 9 selecting the proper organic peroxide and the proper dosing conditions leads to a polymerization reaction where the heat of polymerization is virtually constant over time, which allows optimum reactor space-time yield, very efficient peroxide usage, which results in high polymer yields on the initiator and very low residual peroxide levels in the resin after polymerization.

The only difference between example F of D1 and the teaching of the present claims is, that the second initiator is dosed at a different time, namely from the start on.

No technical effect can be recognized resulting from this technical feature only.

Therefore, it appears, that it was the objective technical problem of the present application to provide an alternative in view of D1.

The claimed solution to this problem is modifying the process of example F in such a way that the second initiator is dosed (at least partly) from the start of the polymerization reaction on, while the closest example of the prior art discloses that it is dosed from a time starting 2,5 hours after the start of the polymerization reaction.

This can not be derived from D1.

Neither can this solution be derived from D1 in combination with any other prior art document on file.

Therefore, an inventive step can be acknowledged.

6. Article 33(4) PCT (Industrial Applicability)

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/EP2004/004500

Since the radical polymerization of olefin is an important industrial process, industrial applicability can be acknowledged to the present claims.

Claims

1. A process to polymerize one or more monomers wherein at most 90 percent by weight of the safely useable amount of a first initiator is used and a second initiator, having a half-life from 0.0001 hour to 1.0 hour at the polymerization temperature and that is less temperature stable than said first initiator, is being dosed at least partially from the start of the polymerization until 10% of the monomer(s) has been polymerized after the start of the polymerization, in an amount, and preferably at a variable rate, such that at least 92% of the maximum cooling capacity is used during at least a period of time wherein at least 10 percent by weight of the monomer is polymerized.
2. A process according to claim 1 wherein the monomers comprise vinyl chloride.
3. A process according to claim 1 or 2 wherein the process is a suspension polymerization process, preferably a batch suspension polymerization process.
4. A process according to any one of claims 1-3 wherein the second initiator is also added intermittently and/or continuously after the start of the pressure drop and/or during the pressure drop.
5. A process according to any one of claims 1-4 wherein a protective colloid is added during the polymerization process.
6. A process according to any one of claims 1-5 wherein said first initiator has a half-life of 0.1 hour to 10 hours at the polymerization temperature and the less temperature stable initiator has a half-life of 0.0001 hour to 1.0 hour at said temperature.



7. A process according to any one of claims 1-6 wherein the amount of the second initiator that is used is at least 0.01% by weight, based on the weight of the monomer that is polymerized.
8. A process according to any one of claims 1-7 wherein the total amount of first and second initiator is 0.01 to 1 %w/w, based on the weight of the monomer that is polymerized.
9. A process according to any one of claims 1-7 wherein the polymerization reactor has a volume of 15 m³ or more.